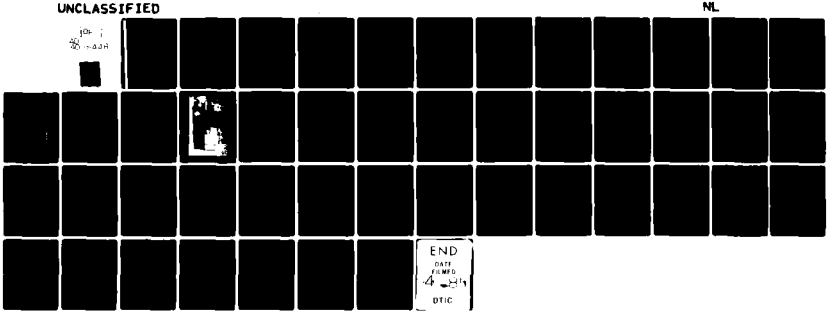
AD-A096 448 ECO INC CAMBRIDGE MA F/G 10/2
ELECTROLYTES FOR HYDROCARBON AIR FUEL CELLS.(U)
JAN 81 M WALSH, F WALSH, D N CROUSE DAAK70-79-C-0165
UNCLASSIFIED NL



Unclassified

ELECTROLYTES FOR HYDROCARBON AIR FUEL CELLS

Final Technical Report

M. Walsh, F. Walsh, D. N. Crouse and R. S. Morris
November 1980

to

U. S. Army Mobility Equipment Research and
Development Command
Fort Belvoir, Virginia

Prepared by

ECO, Incorporated
56 Rogers Street
Cambridge, MA 02142

Contract No. DAAK70-79-C-0165

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A096148	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ELECTROLYTES FOR HYDROCARBON AIR FUEL CELLS		5. TYPE OF REPORT & PERIOD COVERED 9/27/79 - 9/27/80 Final Technical Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) M. Walsh, F. Walsh, D.N.Crouse, R.S.Morris		8. CONTPACT OR GRANT NUMBER(s) DAAK70-79-C-0165
9. PERFORMING ORGANIZATION NAME AND ADDRESS ECO, Inc. 56 Rogers Street Cambridge, MA 02142		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U.S.Army Mobility Equipment Research and Development Command Fort Belvoir, Virginia		12. REPORT DATE January 1981 13. NUMBER OF PAGES 40
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Electrochemistry, Fuel Cell, Electrolytes, Organic Sulfonic Acids

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This research was oriented towards finding an electrolyte with sufficient electrochemical activity and stability to replace phosphoric acid in direct oxidation fuel cells. Commercially available materials received prime consideration. However, ECO's view is that only perfluorocarbon acids promise the necessary thermal, chemical and physical stability. Accordingly, ECO synthesized difluoromethane diphosphonic acid and attempted to

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20] synthesize difluoromethane disulfonic acid. Sufficient quantities of difluoromethane diphosphonic acid were synthesized to permit experimental testing including fuel cell performance data. Difluoromethane diphosphonic acid has: a) twice the ionic conductivity of phosphoric acid. b) thermal stability above 236°C. c) electrochemical stability between 0-1.0V vs. RHE. d) low vapor pressure at 200°C and high viscosity. e) non-corrosive properties toward fuel cell components. f) high rates of electrooxidation of hydrogen and high rates of electroreduction of oxygen.
Further tests are needed to develop data using hydrocarbon fuels for extended periods of time.

Unclassified

ELECTROLYTES FOR HYDROCARBON AIR FUEL CELLS

Final Technical Report

M. Walsh, F. Walsh, D. N. Crouse and R. S. Morris
November 1980

to

U. S. Army Mobility Equipment Research and
Development Command
Fort Belvoir, Virginia

Prepared by

ECO, Incorporated
56 Rogers Street
Cambridge, MA 02142

Contract No. DAAK70-79-C-0165

NOTICE

TABLE OF CONTENTS

(continued)

LIST OF FIGURES

LIST OF TABLES

1.0 Summary

This research was oriented towards finding an electrolyte with sufficient electrochemical activity and stability to replace phosphoric acid in direct oxidation fuel cells.

Commercially available materials received prime consideration. However, ECO's view is that only perfluorocarbon acids promise the necessary thermal, chemical and physical stability.

Accordingly, ECO synthesized difluoromethane diphosphonic acid and attempted to synthesize difluoromethane disulfonic acid.

Sufficient quantities of difluoromethane diphosphonic acid were synthesized to permit experimental testing including fuel cell performance data.

Difluoromethane diphosphonic acid has:

a. Twice the ionic conductivity of phosphoric acid.
b. Thermal stability above 236°C.
c. Electrochemical stability between 0-1.0V vs. RHE.
d. Low vapor pressure at 200°C and high viscosity.
e. Non-corrosive properties toward fuel cell components.
f. High rates of electrooxidation of hydrogen and high rates of electroreduction of oxygen.

Further tests are needed to develop data using hydrocarbon fuels for extended periods of time.

1.1 Program Objective

The objective of this effort was to obtain an electrolyte with sufficient electrochemical activity and stability to replace phosphoric acid in direct oxidation fuel cells.

This was a formidable challenge and has been the subject of intensive research[1-6] by many groups for many years. The eight desired properties[3] of the electrolytes are:

a. Good ionic conductivity
b. Thermal stability to 180°C.
c. Electrochemical stability between 0-1V vs. RHE.
d. Low vapor pressure and high viscosity.
e. Non-corrosive to fuel cell components.
f. Supports high rates of electrooxidation of hydrogen and propane and high rates of electroreduction of air and oxygen.
g. Sufficient surface tension so as not to wet Teflon.
h. Good solvent for reactants and products.

1.2 Technical Approach

In this program, fuel cell performance data were the ultimate criteria for evaluating electrolytes. The performance of each candidate electrolyte was compared to phosphoric acid under the same conditions. At least two separate but identical tests were made to ensure reliable data.

Because this was an electrolyte evaluation program, all tests were made with commercially-available fuel-cell electrodes backed by gold-plated tantalum screens. No effort was made to optimize electrode structure.

The experimental testing included IR free polarization curves for short and long term performance testing. Test

apparatus and procedures are summarized in Section 2.

1.3 Commercially Available Electrolytes

Commercially available electrolytes received prime consideration. However, no commercially available electrolyte appears to meet the program objective.

Commercially available electrolytes have been thoroughly[6] reviewed. Many have been thoroughly studied and found to lack physical and/or chemical stability at 180°C.

ECO's view is that only perfluorocarbon acids promise the necessary thermal, chemical and physical stability at 180°C. This view is based both on the literature[3] and on tests performed on four commercially available electrolytes; namely,

- -methanedisulfonic acid
- -sulfoacetic acid
- -10-dl-camphorsulfonic acid
- -and pentadecafluorooctanoic acid.

These four electrolytes were chosen for test as commercially available representatives of:

- -aliphatic sulfonic acids
- -substituted aliphatic sulfonic acids
- -and perfluorinated carboxylic acids.

Specific results of these tests are summarized in Section 3.

1.4 New Electrolytes

Historically, fuel cell investigations have been limited to materials that can be easily synthesized from a proven preparation scheme. ECO has developed new synthesis routes and has produced difluoromethane diphosphonic acid (DFMDPA) and derivatives of difluoromethane disulfonic acid (DFMDSA). The details of the syntheses are given in Section 4.

2.0 Experimental Procedures and Apparatus

2.1 Fuel Cell Electrodes

Fuel cell performance was measured on commercial electrodes. No attempt was made to optimize electrode structure for a given electrolyte.

The electrode chosen was purchased from Prototech, Inc. (Newton Highlands, MA). This RA-2 electrode is a thin (0.35mm) carbon board which is platinum catalyzed (0.33mgPt/cm^2) on one side and Teflon wet-proofed on the other. Circular test electrodes are cut from these 4"X4" RA-2 electrode sheets using a metal punch. The geometric area of the test electrode exposed to the electrolyte is 5.06 cm^2.

2.2 ECO Half Cell

The first part of this program called for half-cell screening tests of four commercially available electrolytes using oxygen and hydrogen as reactants. These tests were performed on electrodes secured in the electrode holder shown in Figure 1. These holders are milled from blocks of heat-treated Teflon. The holder is plumbed to permit gas flow behind the electrode, and utilizes gold wires for electrical contact to a gold-plated-tantalum screen current collector on the back of the test electrode. The half-cell counter electrode consists of a platinum flag (5 cm^2) with a platinum wire lead. The dynamic hydrogen reference electrode is composed of two $1cm^2$ platinum flags held in a quartz tube, the end of which is drawn out to a capillary.

THE ECO HALF CELL

ELECTRODE HOLDER

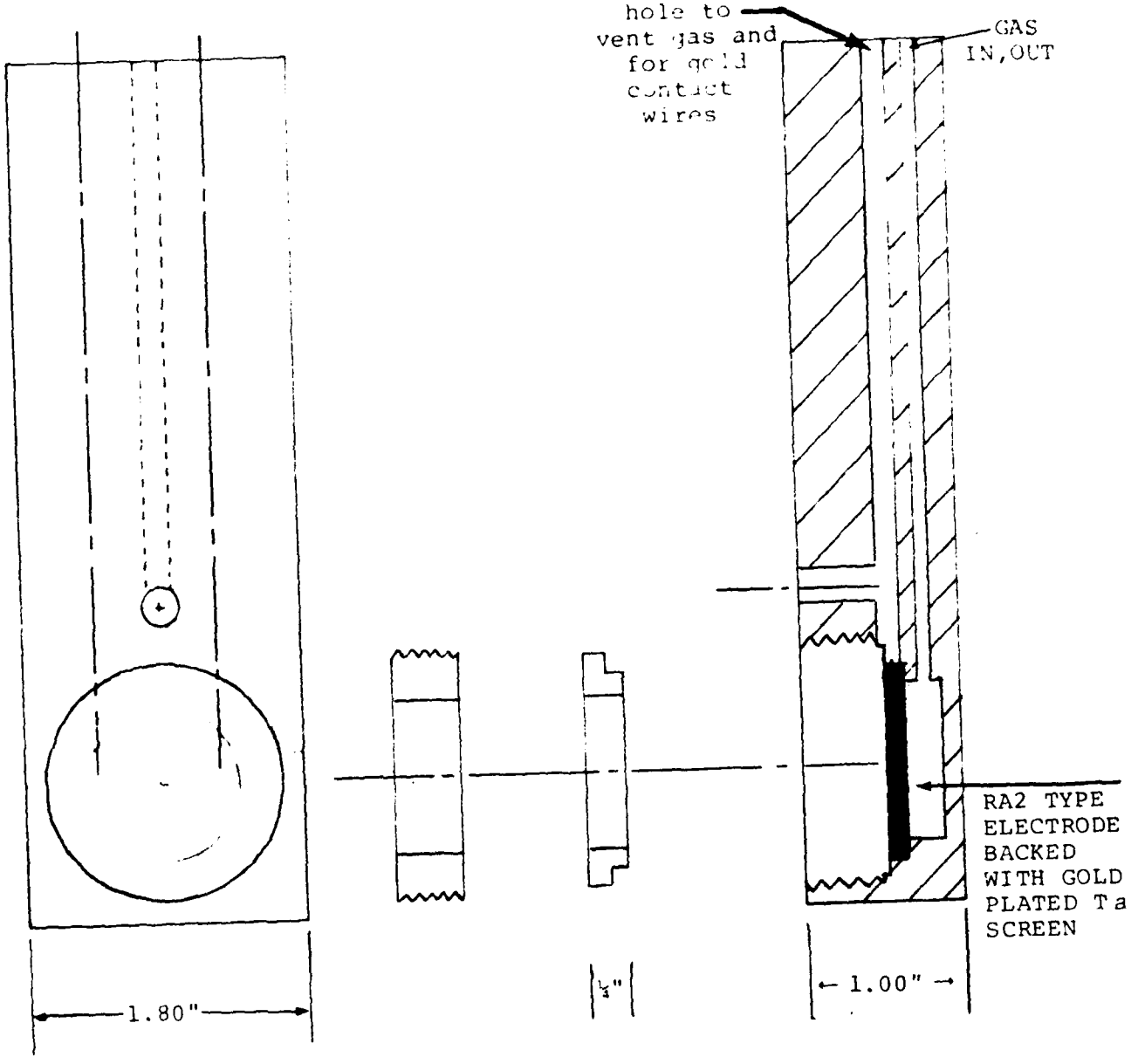


FIGURE 1

The cell case is a rectangular quartz vessel which is placed into a Glas-Col Model TM-614 heat mantle. The temperature is regulated by an Electro-Flex Model 5000R heat controller.

Half-cell tests were run using oxygen and hydrogen as reactants for up to 100 hours each at 100°C. The entire assembly is shown in Figure 2.

2.3 ECO Small Volume Fuel Cell (SVFC)

Early in this contract it was realized that the efforts to synthesize novel organic compounds would probably yield small quantities (< 100 grams) of material. The half-cell apparatus for testing commercially available electrolytes requires 150 grams of material for each half-cell test.

Faced with this dilemma, ECO designed, fabricated, and successfully tested a Teflon fuel cell which requires only 10 grams of electrolyte. Figures 3 and 4 illustrate the ECO small volume fuel cell (SVFC). This cell is, in fact, two ECO half-cells facing one another with cell gases plumbed in from the sides of the cell rather than from the top.

The small volume fuel cell is designed to accommodate two Prototech RA-2 type electrodes backed with gold plated tantalum screens. Gold wires connect the electrodes to the outside world. The reference electrode permits the sequential gathering of voltage and current data from either of the two in-situ electrodes. Consequently, half-cell data can be gathered while running the electrolyte in the fuel

cell mode.

The reference electrode used in the SVFC was a dynamic hydrogen electrode and consisted of a 0.02" thick platinum wire ring anode (located at position A in the reference electrode well), and a 1 cm^2 platinum cathode (the DHE) suspended in the electrolyte at the bottom of the cell.

As in the case of the ECO half-cell apparatus, temperature regulation was accomplished by placing the entire SVFC into the Glas-Col heat mantle, and maintaining the desired temperature using an Electro-Flex Model 5000R heat controller.

2.4 Electronic Apparatus and Gas Systems

An ECO Model 552 potentiostat was employed to obtain the IR free Tafel slope data. This potentiostat has a built-in IR compensation circuit, which enables the experimentor to overcome ohmic drop across the cell. During steady state periods, the cell voltages were maintained to $\pm$ 0.001V by a Heathkit Model IP-18 power supply.

The hydrogen, oxygen and nitrogen used were 99.995% purity and were obtained from Med-Tech Gases (Medford,MA). All plumbing was either copper, brass, or Teflon. Gases were normally used without humidification.

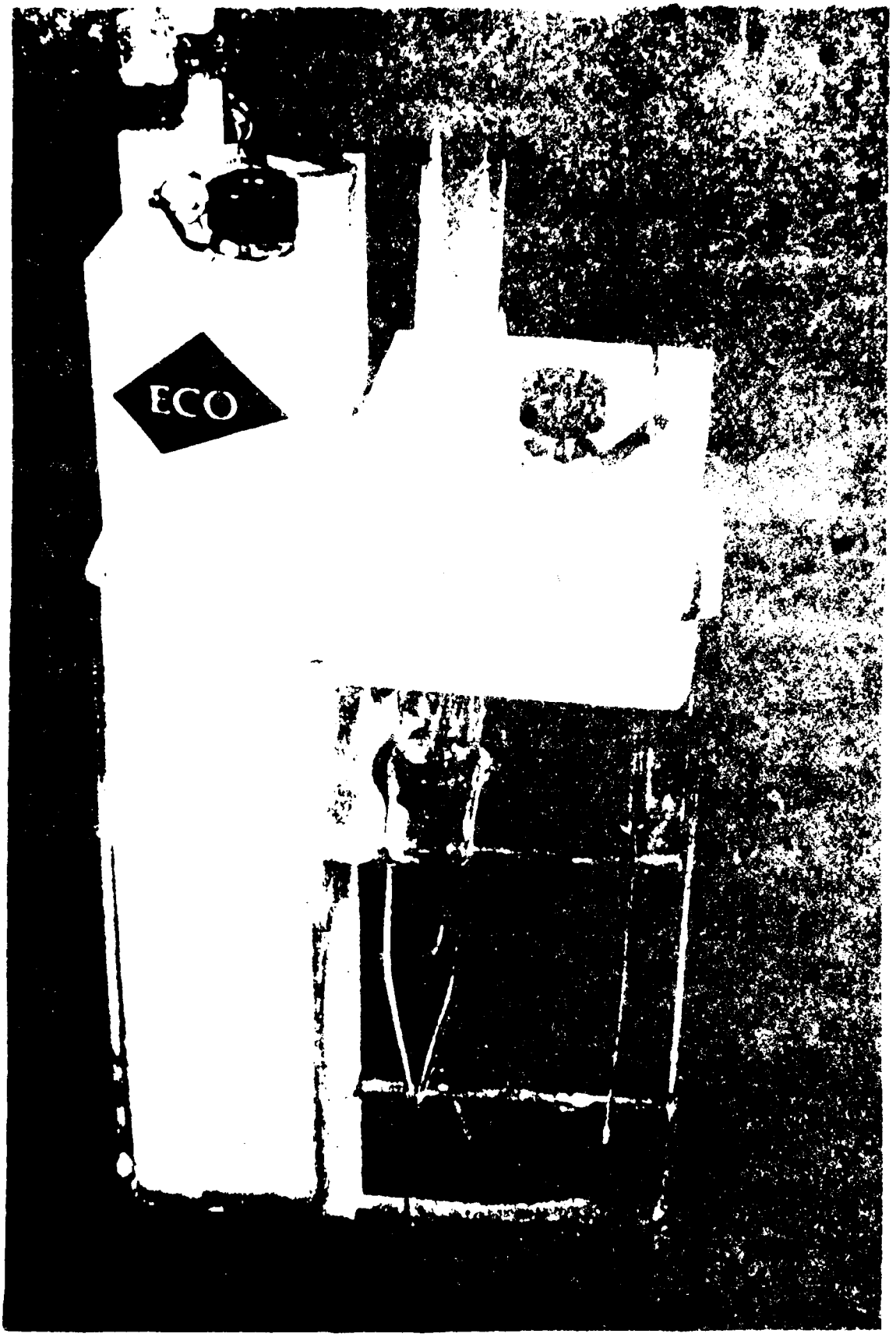
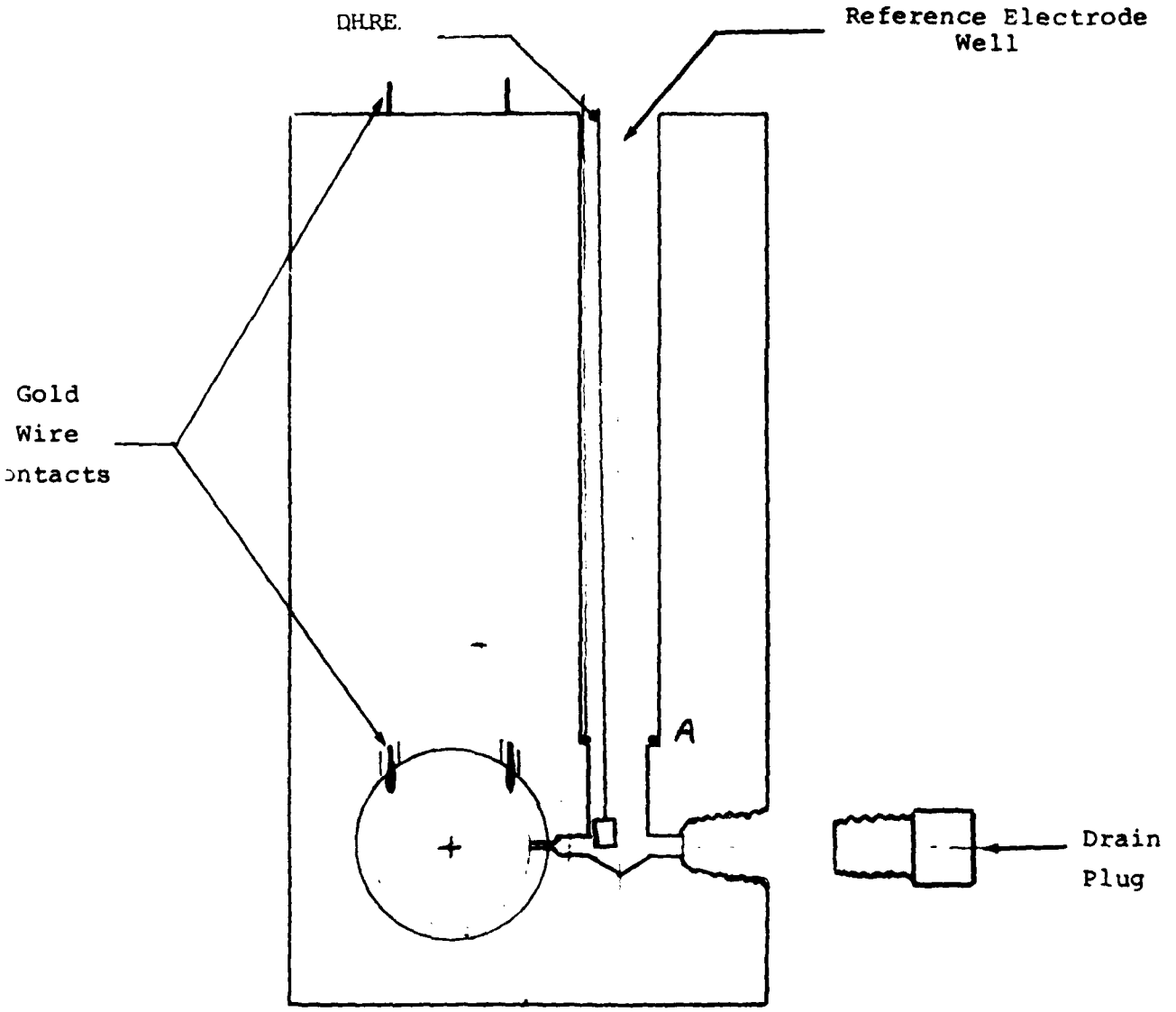


FIGURE 2

ECO Small Volume Fuel Cell

Figure 3



ECO Small Volume Fuel Cell

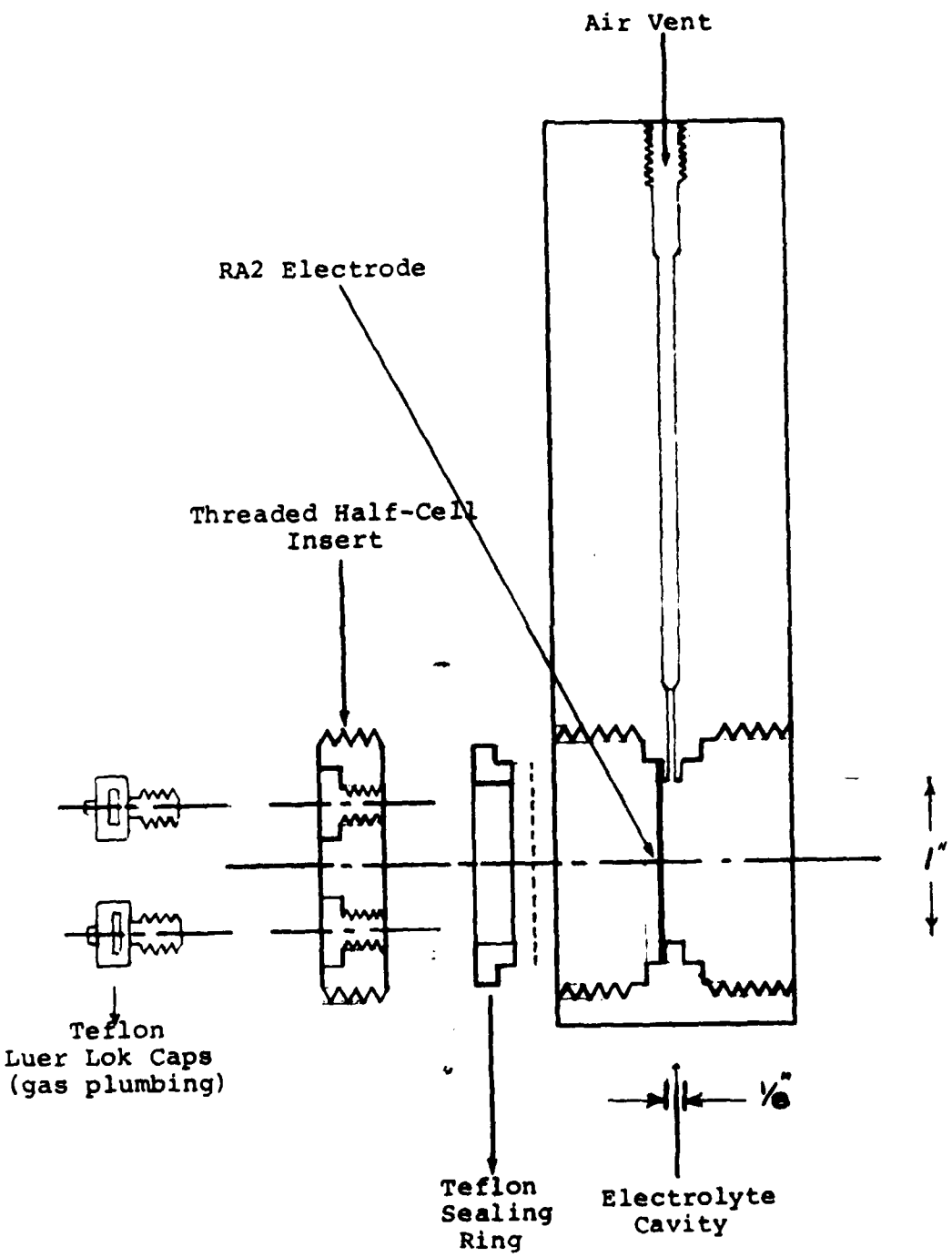


Figure 4

3.0 Commercially Available Electrolytes

The data and recommendations found in the work of ERC[4], Argonne National Laboratory[5], and The American University[6] and EIC[7] were carefully reviewed. This work spans more than eight years and appears to cover every important commercially available electrolyte. All appear to lack at least one critical property.

ECO selected and tested four commercially available electrolytes to learn first-hand the problems associated with sulfonic acids and perfluorinated carboxylic acids. These acids do not have sufficient physical and/or chemical stability at 180°C to merit further study.

3.1 Phosphoric Acid

The performance of each candidate electrolyte is compared with phosphoric acid under the same conditions. Figure 5 illustrates the IR free performance of Mallinckrodt 85% phosphoric acid at various temperatures in the ECO small volume fuel cell. The reversibility of the hydrogen electrode and the oxygen Tafel slope of about 120mV/decade together demonstrate that the ECO fuel cell is working properly. Dry gases are used throughout the tests.

At higher temperatures, the phosphoric acid "dries out" and cell decay is quite rapid. Figure 6 illustrates this effect. This limits phosphoric acid to lower temperatures or to pressurized humidified gases.

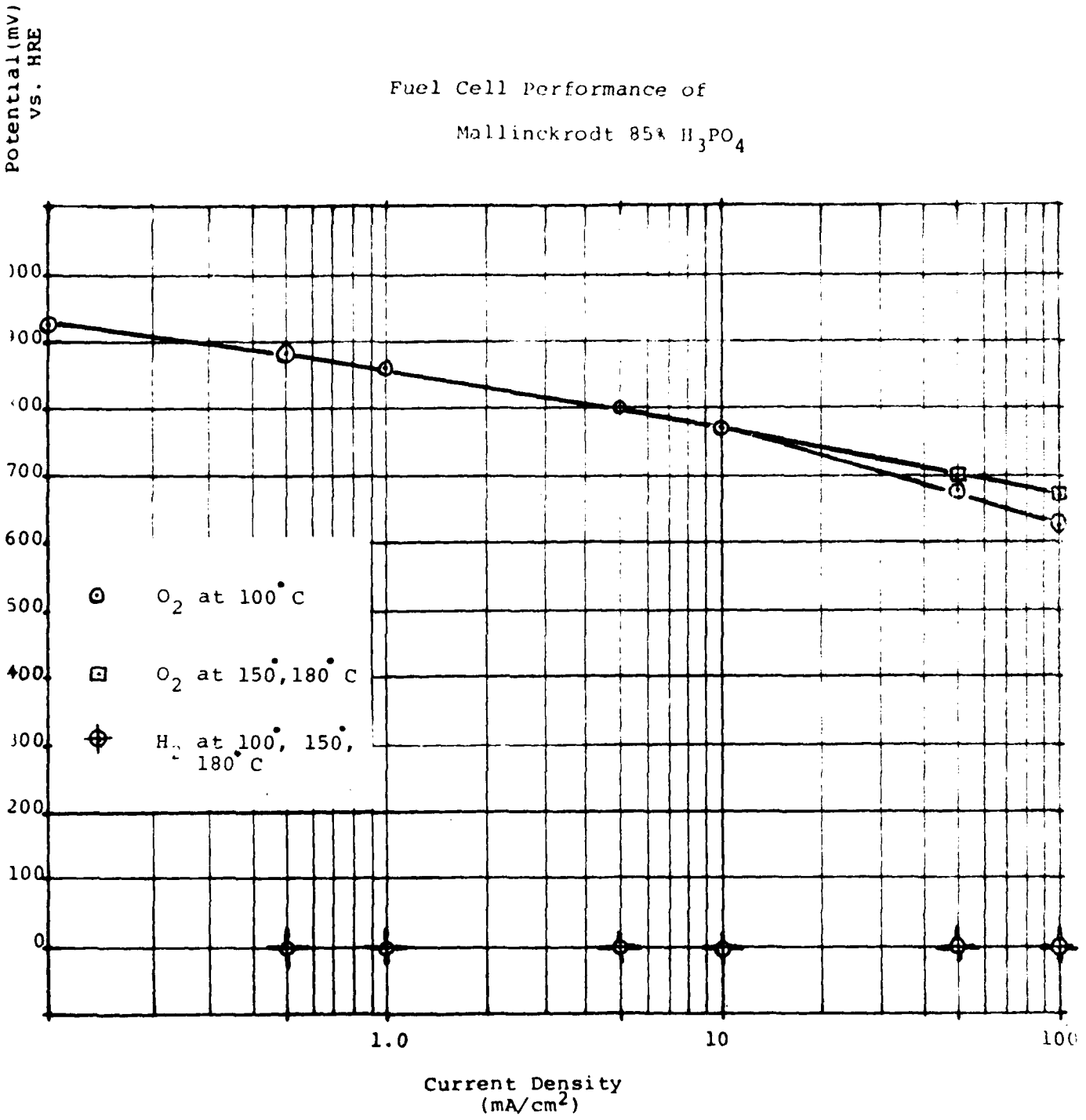

Potential(mV) vs. HRE
Fuel Cell Performance of
Mallinckrodt 85% H_3PO_4
700
600
500
400
300
200
100
0
O_2 at 100° C
O_2 at 150°, 180° C
H_2 at 100°, 150°, 180° C
1.0
10
100
Current Density
(mA/cm²)

FIGURE 5

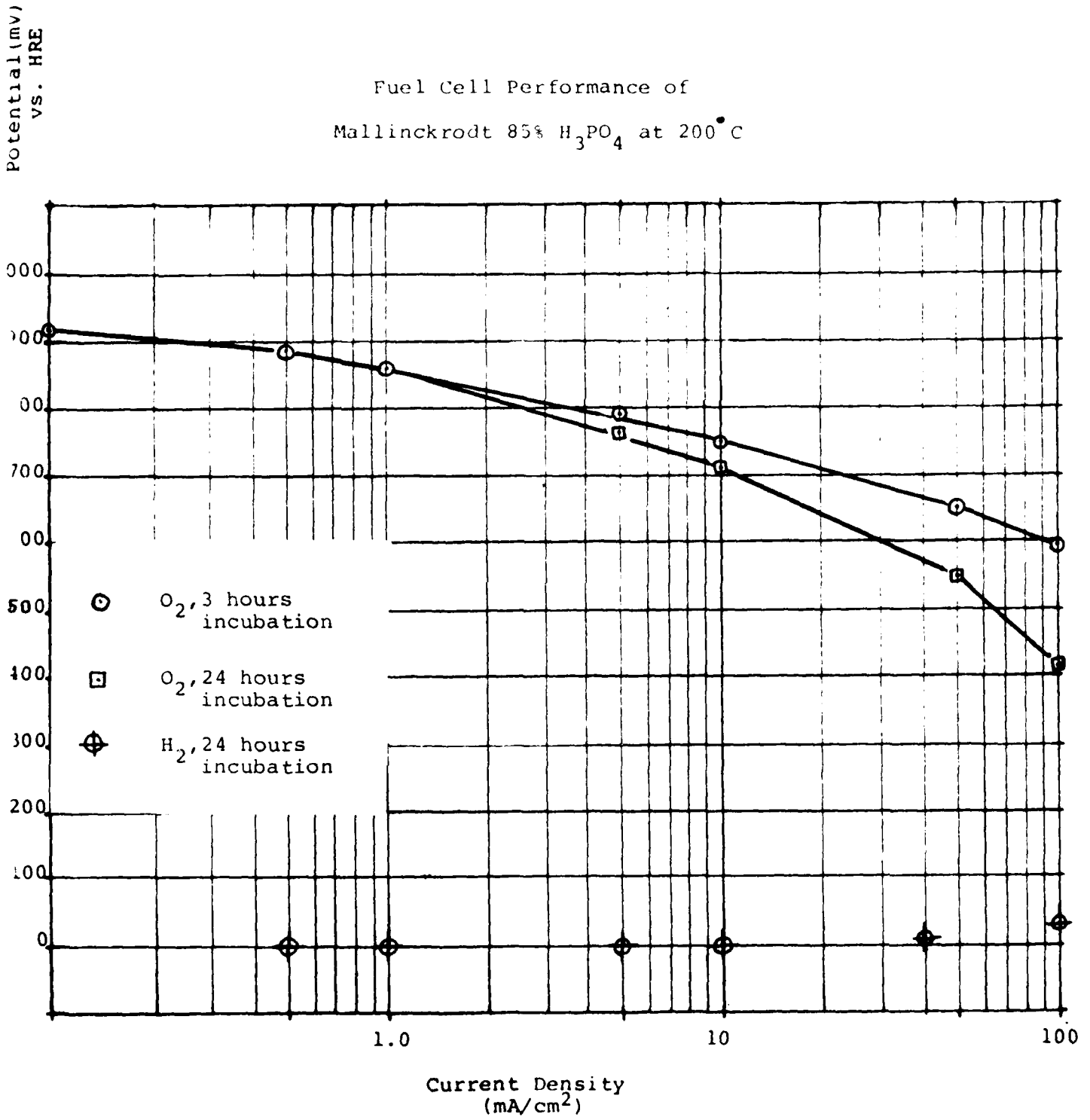

Potential(mV) vs. HRE
Fuel Cell Performance of
Mallinckrodt 85% H_3PO_4 at 200°C
000
00
00
700
00
500
400
300
200
100
0
O_2, 3 hours incubation
O_2, 24 hours incubation
H_2, 24 hours incubation
1.0
10
100
Current Density (mA/cm^2)

FIGURE 6

3.2 Aliphatic Sulfonic Acids

Aliphatic sulfonic acids are, in general, inert towards strong oxidizing agents. They are very stable to heat, acid, and alkali. Yet, methionic acid,(or methanedisulfonic acid $CH_2(SO_3H)_2$ was investigated by ERC[4] in fuel cells and was a terrible electrolyte. ERC observed "desulfonation" at 130° C.

Since ECO is synthesizing $CF_2(SO_3H)_2$, and since "desulfonation" is apparently[8] not a problem[1] with $CF_3(SO_3H)$, ECO investigated the behavior of $CH_2(SO_3H)_2$ in half cells.

The oxygen half-cell performance of methanedisulfonic acid at 100° C is shown in Figure 7. The electrolyte in the oxygen half-cell appeared unchanged. The performance was steady and there were no indications of chemical decomposition except at the dynamic hydrogen reference electrode.

This experiment was repeated with a hydrogen half-cell. No meaningful performance curve resulted. The electrolyte rapidly darkened and there was a noticeable odor of H_2S. A yellow colored crystalline material formed around the cooler edges of the quartz test cell. This material was collected and found to be insoluble in methanol, to be quite soluble in CS_2, and to contain no acidic protons. This suggests that methanedisulfonic acid at 100° C is easily reduced at a platinum/hydrogen anode.

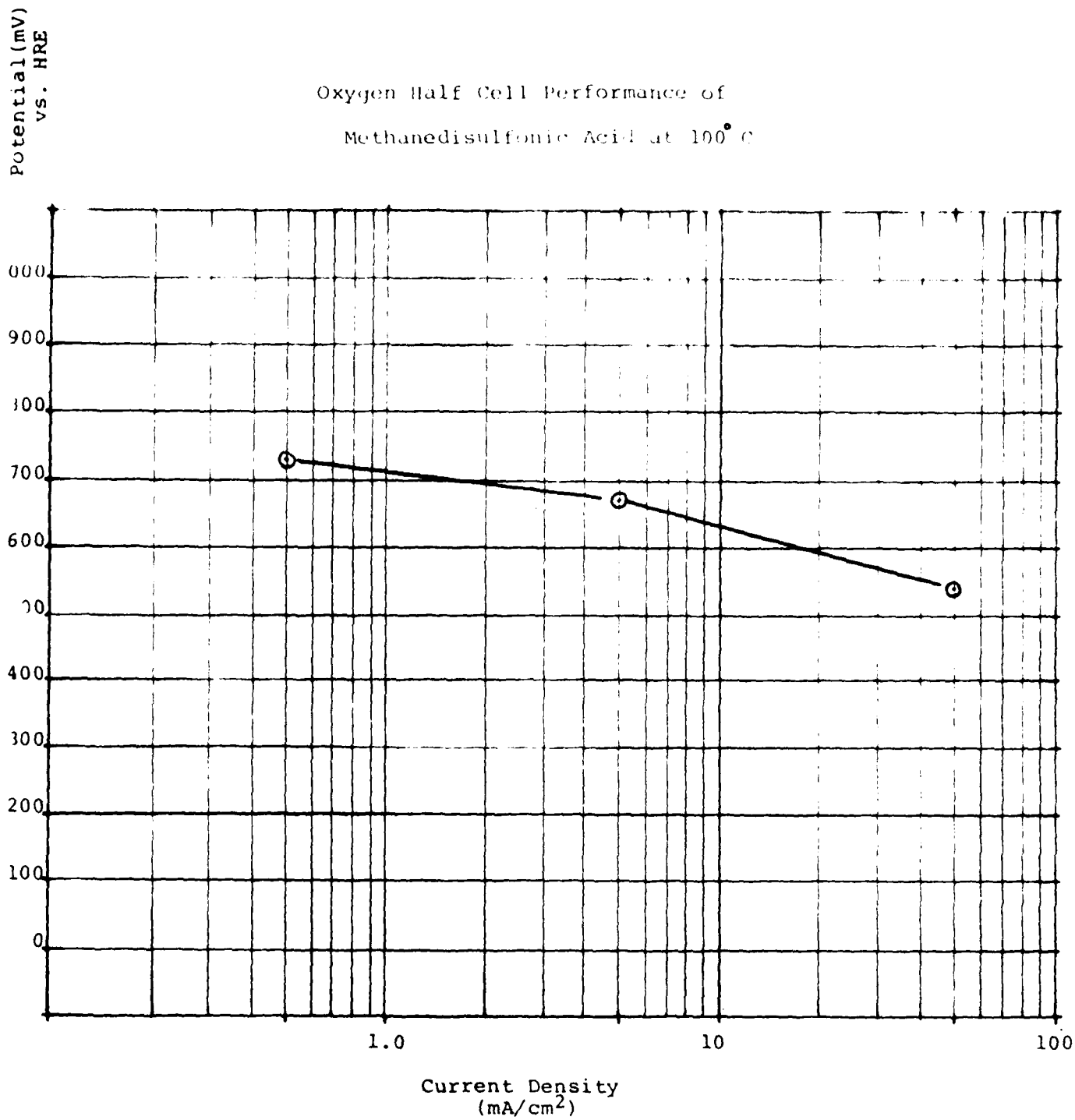

Potential(mV) vs. HRE
Oxygen Half Cell Performance of
Methanedisulfonic Acid at 100° C
000
900
300
700
600
00
400
300
200
100
0
1.0
10
100
Current Density
(mA/cm2)

FIGURE 7

Unsubstituted aliphatic sulfonic acids are, therefore, unsuitable as fuel cell electrolytes. Presumably, substitution of fluorine protects the SO_3H group in $CF_3(SO_3H)$.

3.3 Substituted Aliphatic Sulfonic Acids

Substitutions in the hydrocarbon chain can increase the stability of aliphatic sulfonic acids. Sulfoacetic and dl-10-camphorsulfonic acids were tested and found to decompose thermally.

Sulfoacetic acid thermally decomposes at 180° C apparently due to decarboxylation. This is substantially below the 245° C reported by previous workers.[6]

dl-10-camphorsulfonic acid decomposes at its melting point of 193° C.

With the possible exception of fluorinated substituted aliphatic sulfonic acids, substituted aliphatic sulfonic acids are unsuitable as fuel cell electrolytes. The promise of the perfluoroalkane sulfonic acids was recognized[3] in 1974.

3.4 Perfluorinated Carboxylic Acids

Perfluorinated carboxylic acids have been suggested[5] as interesting electrolytes. A typical member of this family, pentadecafluorooctanoic acid, boils at 187°-189° C and melts at 53° C.

However, after incubating pentadecafluorooctanoic acid at 55°C for 16 hours, roughly one quarter of the acid had evaporated. This reflects a very high vapor pressure at the melting point.

It is likely that high vapor pressure will make perfluorinated carboxylic acids unacceptable long before thermal decarboxylation takes place.

4.0 Syntheses of New Electrolytes

The program objective requires an electrolyte with eight very specific properties. ECO's approach is to synthesize compounds which can have these properties, rather than to select compounds primarily because they are commercially available.

For chemical stability and electrochemical activity,[9] the electrolyte must have no carbon-hydrogen bonds. So as not to wet Teflon, the oxygen to fluorine ratio should be greater than one. The electrolyte must have a very low vapor pressure at 200°C and should be made by a short high-yield synthesis from inexpensive starting materials.

These conditions can all be met with perfluorocarbon bis-acids. Since the thermal stabilities of fluorosulfonic and fluorophosphonic acids are known to be high and usually exceed 200°C, these are good groups to consider.

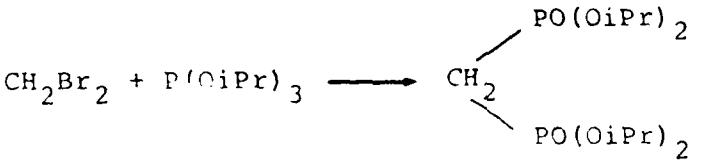
There are numerous possible acids. However, dissymmetry always means extra synthetic steps and the greater the number of fluorine atoms per molecule, the higher the cost. Hence, among candidates considered potentially suitable as fuel cell electrolytes are difluoromethane diphosphonic acid (DFMDPA) and difluoromethane disulfonic acid (DFMDSA).

4.1 Synthesis of Difluoromethane Diphosphonic Acid

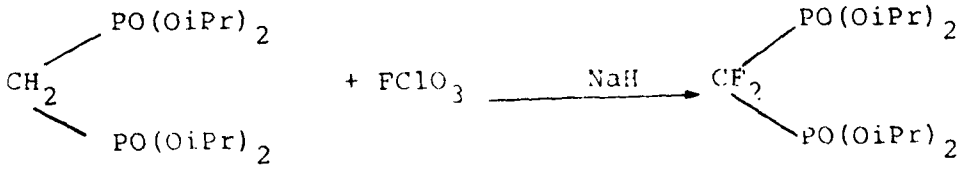
Difluoromethane diphosphonic acid (DFMDPA) was synthesized by a route developed for the Energy Power Research Institute (EPRI) under contract RP 1676-1-1. The synthesis of DFMDPA begins

with the reaction between dibromomethane and triisopropyl phosphite to afford the tetraisopropyl ester of methane diphosphonic acid. Treatment with sodium hydride and perchloryl fluoride resulted in the tetraisopropyl ester of DFMDPA. This second step was found to be extremely hazardous, resulting in several explosions. Stringently enforced safety precautions minimized personal injury.(At the present time we are seeking alternative means of fluorination.) The ester was hydrolyzed with concentrated hydrochloric acid to crude DFMDPA. Purification was carried out by conversion of the acid to its acid chloride with phosphorous pentachloride, fractional distillation of this chelate and hydrolysis back to pure DFMDPA.

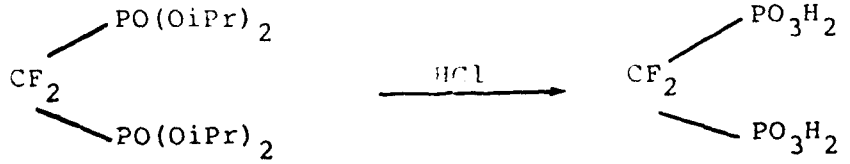
This route can be represented as:



(1)



(2)



(3)

A portion of the tetrasodium salt of the crude DFMDPA was sent out for toxicological testing. DFMDPA is a potentially toxic material due to its similarity to pyrophosphate. The results reveal that 2500-5000 mg per kg of body weight cause death in the test rats.

The detailed procedure for the synthesis of DFMDPA follows.

4.1.1 Preparation of Tetraisopropyl Methylene Diphosphonate

The procedure of C.H. Roy [U.S. Pat. 3,251,907(1962)] was followed. Triisopropyl phosphite (89-90% from Mobil Chemicals, Richmond,VA) was distilled over sodium metal under high vacuum. The impurities which were removed were 3% diisopropyl hydrogen phosphite and 6% of the higher boiling triisopropyl phosphate.

The distilled triisopropyl phosphite (3 moles, 624g) and dibromomethane (1 mole, 174g from Aldrich Chemical Co.) were placed in a 1 liter three-necked flask fitted with a submerged thermometer, a thermocouple, a magnetic stirrer, a heating mantle controlled by a thermostat, and a Liebig condenser. The Liebig condenser was fitted with a Dean-Stark trap; this, in turn, was fitted with a water-cooled Friedrich condenser, with an outlet for gases through a calcium chloride drying tube.

The Liebig condenser was packed with glass helices (1/8" diameter) over the entire length of the jacket, and was maintained at 60°-70°C with a recirculating Blue M water heater. The Dean-Stark trap (excluding the collection tube) was wrapped with heating tape and also was maintained at 60°-70°C.

Heat was applied to the reaction mixture by setting the mantle thermostat at 140°C for 2 hours. The temperature was gradually increased to 160°C for an additional 8-18 hours. The uptake of starting material was monitored by NMR.

During the reaction, isopropyl bromide (~200ml) accumulated in the Dean-Stark trap. Heating to higher temperatures (180°C according to Roy's patent) led to polymer formation. After the reaction mixture cooled, it was transferred to a distillation apparatus and distilled under high vacuum from $NaHCO_3$. Sufficient $NaHCO_3$ was added (2-4g) so that some remained after gassing had ceased. Two fractions were taken:

-triisopropyl phosphite (40°C,0.3mm)

-diisopropyl bromomethylene phosphate mixed with diisopropyl/isopropyl-phosphonate(80-140°C,0.3mm)

The distillation was continued at a bath temperature of 160°C at 0.3mm until the pot residue contained 1% diisopropyl bromomethylene phosphonate (as determined from NMR- bromomethylene doublet at 3.30ppm, J_{PH}=10Hz, in CCl_4) and tetraisopropyl methylene diphosphonate.

During the preparation and distillation of tetraisopropyl methylene diphosphonate, there was some thermolysis to propylene and free acid, particularly at temperatures greater than 160°C. To remove all traces of acid, the pot residue (~300g) from the previously described distillation was diluted with 300ml of a 1M phosphate buffer(pH=6.88) followed by saturated aqueous bicarbonate to adjust the pH to 7.0; gas evolution was noted.

This aqueous solution was extracted 3 times with ethyl ether (total volume 1 liter) and the ether layer was dried over magnesium sulfate. The ether was stripped off and the residue dried by azeotroping with benzene. This produced a cloudy suspension which was diluted with anhydrous ethyl ether, filtered and then stripped. The tetraester is capable of forming a stable hydrate with water. The water appears as a singlet at approximately 3.40ppm in proton NMR.

The NMR of tetraisopropyl methylene diphosphonate in CCl_4 shows peaks at 1.28ppm (doublet, 12H-CH_3, J_{ch}=6Hz), 2.23ppm (AB-quartet or triplet, 2H-CH_2,J_{PH}=21Hz), and 4.70ppm (sextet of doublets, 4H-CH, J_{HH}=6Hz, J_{PH}=2Hz).

The IR spectrum of methylene diphosphonate (neat,NaCl) shows C-H bands at 3010, 2960 and 2900 cm^{-1} with a strong P=O band at 1240-1280 cm^{-1} and a strong broad band at 810-835 cm^{-1}.

The mass spectrum at 180°C source temperature with 70eV electron beam shows a parent ion at 344 with a strong P+1 at 345, along with strong peaks at 329 (loss of CH_3), 303 (loss of propene radical), and 285 (loss of isopropoxy).

4.1.2 Preparation of Tetraisopropyl Difluoromethylene Diphosphonate

A 1 liter three-necked round-bottomed flask was fitted with a mechanical stirrer, a submerged gas inlet tube, a submerged glass-coated thermocouple, a water condenser and a gas outlet. The gas outlet was fitted with a 500ml trap and terminated by

submersion in a KOH-EtOH solution. The gas inlet line was fitted with two "T's" which permit the introduction of either nitrogen or perchloryl fluoride and which inhibit pressure build-up by using a mercury check-valve.

The apparatus was flushed with argon. Sodium hydride (50% in mineral oil, 48g, 1.0M, from Ventron) was added and washed three times with pentane under an argon atmosphere. The gas inlet tube was replaced with a septum and the gas outlet tube was connected to a vacuum line to produce a partial vacuum and thus remove the last traces of pentane. After the pentane was removed, the apparatus was vented carefully with argon through the septum and the gas outlet line which is submerged in the KOH-EtOH solution.

Tetrahydrofuran (THF) [300ml, dried and distilled from benzophenone sodium ketyl] was added to form a slurry. The flask was fitted then with an ultrasonic bath filled with carbon tetrachloride and dry ice. The slurry was cooled to -10°C and with sonification and stirring, a solution of THF (50ml,dry, distilled) and tetraisopropyl methylene diphosphonate (50.0g, 0.145moles) was added slowly. The temperature was kept below 0°C and foaming was controlled due to escaping hydrogen. After this addition was completed and gassing subsided, the septum was removed and replaced with the gas inlet line; argon flow was continued. A safety shield was placed in front of the reaction vessel. The pyrometer and gas controls (perchloryl fluoride and argon) were positioned in such a way as to minimize operator

exposure to the potentially explosive reaction. The operator must control gas flow, monitor temperature, check pressure build up (mercury check-valve) and monitor gas flow (at KOH-EtOH solution) with minimized risk of injury.

When the mixture had cooled to -10°C, the argon flow was stopped and perchloryl fluoride was introduced at a slow, steady flow. The exothermic reaction may get out of control easily unless the temperature is maintained between -10° and 0°C by adjusting the flow rate. It may become necessary to stop the flow of perchloryl fluoride completely at some point; if this is the case, the system should be vented with argon at the same slow rate as that rate at which the perchloryl fluoride was introduced. It is important to keep some gas flowing at all times because the inlet tube has a tendency, otherwise, to plug.

As the reaction proceded, the temperature decreased and was maintained at -10° to 0°C by increasing the gas flow until the temperature fell below -10°C. The flow of perchloryl fluoride was then stopped and the system was vented with argon and allowed to warm to room temperature. With a continued flow of argon, the resulting slurry was filtered carefully under an argon atmosphere and behind a safety shield. The operator wore heavy gloves and used a large sintered glass funnel with a cellulose filter aid and a presovac pump to provide a partial vacuum. The filter cake was washed with dry, distilled THF and then carefully quenched with isopropanol. The resulting THF solution was stripped and resuspended in dry benzene, filtered,

and evaporated, resulting in a lightly colored oil (49-53g, 88-96%). PNMR was run for a purity check (triplet,209.96Hz, J_{FP}=79 Hz, 65-90% signal).

4.1.3 Preparation and Purification of DFMDPA

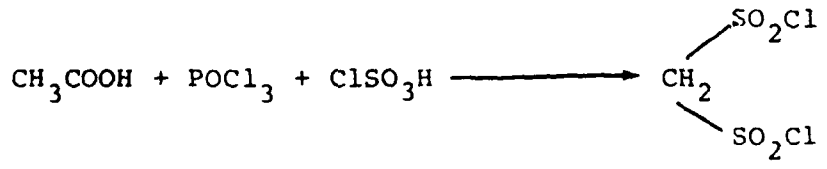
The tetraisopropyl difluoromethane diphosphonate (37.0g, 97mmoles) was treated with concentrated hydrochloric acid (10N,111ml) and stirred to form a milky suspension. Upon refluxing, a clear solution was obtained. After refluxing for 3 hours, the mixture was cooled and the water, isopropanol, and hydrochloric acid were removed under vacuum. The resulting hygroscopic oil was used directly in the next step. While cooling the flask in an ice bath with mechanical stirring, the oil was treated with phosphorous pentachloride (202g, 0.97 moles) over a 3 hour period. The resulting suspension was allowed to warm to room temperature and was stirred an additional 18 hours.

The liquid was decanted carefully from any unreacted phosphorous pentachloride and was distilled to remove phosphorous oxychloride. The residue from this distillation contained 30ml solid phosphorous pentachloride and was filtered through a cellulose filter aid. The resulting liquid was distilled to yield 5.4g difluoromethylene-bis-phosphonic acid dichloride (bp 65°C/1mm, 20% yield over the two steps). This material is free from unfluorinated and monofluorinated derivatives as verified by PNMR (a clear triplet, 775.14 Hz, J_{FP}= 105 Hz).

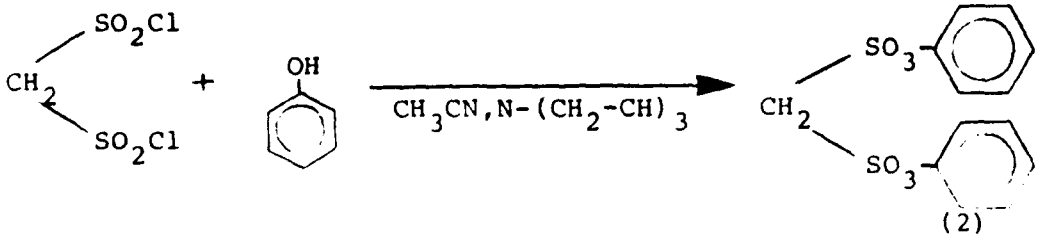
The acid was regenerated by the addition of the bis-diphosphonic acid dichloride (1.0g,3.5mmoles) to water (10ml), dropwise, while stirring. A cloudy solution was formed which was stirred at room temperature for 18 hours. The resulting clear solution was stripped of water and hydrochloric acid and placed under high vacuum, producing a clear semisolid acid (0.72g,98%). This material is shown to be free from acid chloride and other fluorinated derivatives through PNMR of its tetramethyl ammonium salt (triplet, 209.96, J_{FP}=79Hz, 99% of signal).

4.2 Synthesis of Difluoromethane Disulfonic Acid

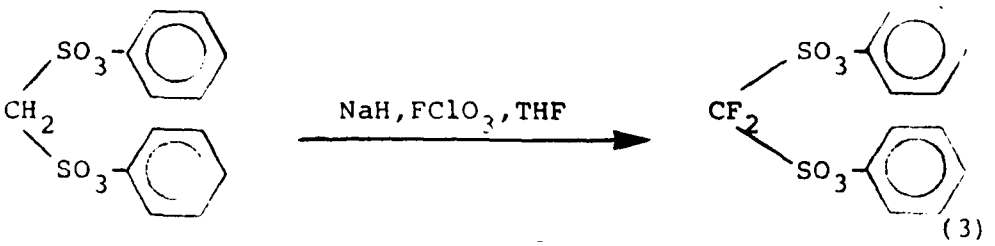
The diphenyl ester of difluoromethane disulfonic acid (DFMDSA) could be prepared from the diphenyl ester of methane disulfonic acid by the same fluorination technique as that used for DFMDPA. The synthesis route for DFMDSA is:



(1)



(2)



(3)

ECO has developed this route which prepares diphenylmethane disulfonate by the utilization of acetic acid, instead of methylene bromide, as a starting material. This differs from EIC's route.[7]

ECO's route permits the production of the bis sulfonyl chloride in one step (as opposed to the two steps required by the EIC route). ECO's preparation of crystalline methane bis sulfonyl bis phenol ester from bis sulfonyl chloride is also a unique procedure which requires inexpensive triethylamine as an organic soluble base.

The fluorination step is hazardous and ECO experienced a severe detonation when using potassium hydride instead of sodium hydride. The hydrogen-fluorine exchange is achieved in one step. This ester strongly resists hydrolysis. Attempts to convert the ester to the free acid with acetic, hydrochloric, and nitric acids have failed. No conditions were found for ester hydrolysis which did not result in the decomposition of the starting material (see Table I). Some attempts at circumventing this problem, by using other derivatives of DFMDSA prepared in these laboratories, are shown in Table II. The diisopropyl ester of methane disulfonic acid was prepared, but could not be fluorinated with perchloryl fluoride.

TABLE I

RESULTS OF ATTEMPTS TO HYDROLYZE ESTER

No Reactions took place when the diphenol ester of difluoromethane disulfonic acid was refluxed for:

- 3 hours in 5% HF/H_2O
- 24 hours in conc. HCl
- 24 hours in conc. HCl/EtOH
- 36 hours in HNO_3/AcOH
- 1 hour O_3/MeOH followed by conc. HCl/EtOH

No Reactions took place when the di o-methoxy phenol ester of difluoromethane disulfonic acid was refluxed in:

- HCl/AcOH
- H_2/Pt/carbon EtOH
- O_3/EtOH,0°C followed by H_2/Pd, $BaSO_4$,0°C

Decomposition of the diphenol ester and the o-methoxy phenol ester took place at the carbon-sulfur bond in:

- NaOEt/EtOH
- NaOH/Dioxan/H_2O
- $NaOCH_3$/Sulfolane

TABLE II

ELEVEN UNSUCCESSFUL ATTEMPTS TO SYNTHESIZE DFMDSA

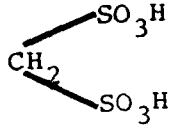
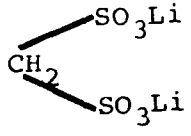
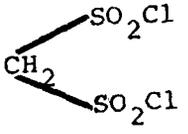
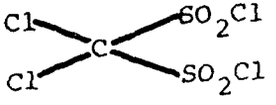
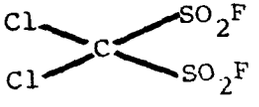
STARTING MATERIAL	CONDITIONS	RESULTS
	$LiOH/H_2O$	salt insoluble in THF and DMF
	$NaOH/H_2O$	salt insoluble in THF and DMF
	Tetramethyl ammonium hydroxide/H_2O	salt insoluble in THF and DMF
	PCl_5	No product isolated

TABLE II

STARTING MATERIAL	CONDITIONS	RESULTS
	$NaOCH_3$/THF	No distillable product isolated
	o-methoxy phenol/ Et_3N acetonitrile	36% o-methoxy derivative of diphenyl ester
	p-methoxy phenol/ Et_3N acetonitrile	75% p-methoxy derivative of diphenyl ester
	N-chlorosuccinimide/ thionyl chloride	36-50% dichloromethane disulfonyl chloride
	KF/18-Crown-6- ether acetonitrile	50% dichloromethane disulfonyl fluoride
	KF/18-Crown-6-ether sufulane	No product isolated
	$(n\text{-butyl})_4\overset{+}{N}F^-$ /H_2O	No product isolated

4.2.1 Preparation of Methane Disulfonyl Chloride

To a three-necked round-bottomed flask under nitrogen, fitted with a thermometer, an addition funnel, and a water condenser vented to a water trap was added chlorosulfonic acid (116.6g, 1.0 mole) followed by phosphorous oxychloride (153g, 1.0 mole). This mixture was stirred magnetically and cooled in an ice bath. To this solution was added dry, distilled acetic acid (30g, 0.5 moles), dropwise. After addition, the mixture was heated to 105°-110°C. When the phosphorous oxychloride ceased to reflux (approximately 2 hours), the mixture was heated to 140°-145°C for 5 hours. A clear, viscous oil was produced which stopped stirring after 1/2 hour. The mixture was cooled and decanted from the viscous oil. The dark mobile liquid was distilled to yield methane disulfonyl chloride (78.8g, bp 101°-104°C/1.5mm). NMR (neat) shows a singlet at 5.7ppm.

4.2.2 Diphenyl Methane Disulfonate

In a three-necked round-bottomed flask, fitted with a water condenser, a mechanical stirrer, and an addition funnel was placed methane disulfonyl chloride (192.5g, 0.9 moles) and phenol (170g, 1.8moles) in acetonitrile (1.5 liters). To this stirred solution was added triethyl amine (182g, 1.8 moles); the temperature was allowed to rise slowly to 60°C. After addition was completed, the mixture was stirred at ambient temperature for one hour. This mixture was poured into

1.5 liters of water which formed an oil and separated from the water. The oil was dissolved in THF and sufficient ethyl ether was added to form two layers with the water. The mixture was washed twice with water.

The organic phase was stripped to yield a crystalline product which was recrystallized twice from toluene-pentane. Diphenyl methane disulfonate was obtained (148.8g, mp 78°-80°C, 50% yield). NMR ($CDCl_3$) shows a singlet at 7.45ppm (10H) and a singlet at 4.85ppm (2H).

4.2.3 Preparation of Difluoromethane Disulfonic Acid Diphenyl Ester

In the same apparatus used previously for fluorination was placed sodium hydride (51.0g, 1.06moles, 50% in mineral oil, Ventron). This was washed with pentane and dried.

The sodium hydride was suspended in dry, distilled THF (500ml) and cooled in an ultrasonic bath with carbon tetrachloride and dry ice to -10°C. To this was added a solution of THF (50ml) and diphenyl methane disulfonate (50.0g, 0.152 moles) via syringe. The temperature was maintained between -10°C and 0°C. Following safety precautions described earlier in the synthesis of DFMDPA, this solution was treated with perchloryl fluoride which produced an exothermic reaction which was controlled to between -10° and 0°C.

When this reaction subsided and the temperature dropped below -10°C, the addition of perchloryl fluoride was stopped

5.0 Test Results on DFMDPA

Measurements were made to determine the ionic conductivity, chemical stability, electrochemical stability, vapor pressure, wetting characteristics and fuel cell performance of DFMDPA.

DFMDPA has excellent ionic conductivity, chemical stability, electrochemical stability and wetting characteristics. Pure DFMDPA supports high rates of electrooxidation of hydrogen. However, the cathode performance in oxygen of DFMDPA is no better than that of phosphoric acid. Also, DFMDPA appears to codistill with water vapor at temperatures less than 140°C. At higher temperatures, DFMDPA appears to polymerize and its vapor pressure becomes very small. Fuel cells with dry hydrogen and oxygen were successfully operated at 236°C for 24 hours.

5.1 Contact Angle Measurements

DFMDPA does not wet Teflon.

The contact angle for treated pure DFMDPA is 99.4°. The contact angle for Mallinckrodt 85% ortho-phosphoric acid under identical conditions is 114.0°.

Contact angle measurements were performed on pure DFMDPA at room temperature, atmospheric pressure, with no provisions made for humidifying the electrolyte, using a Gaertner M 101 telescope with a M205 protractor eyepiece. The DFMDPA was placed on a flat piece of PTFE and the goniometer apparatus was pre-calibrated using a variety of organic solvents, and by comparing contact angle results with those of Fox and Zisman.[10]

5.2 Conductivity

The specific conductance of 85% DFMDPA was measured at temperatures up to 120°C. These data are shown below. It appears that DFMDPA is twice as conductive as phosphoric acid.

TABLE III

Conductivity Measurements ($ohm^{-1}cm^{-1}$)

Temperature	85% H_3PO_4	85% DFMDPA
20°C	.064	.153
40°C	.107	.201
60°C	.131	.247
80°C	.165	.311
100°C	.183	.357
120°C	.201	.384

5.3 Physical Stability

DFMDPA appears to codistill with water in a manner very similar to the behavior of ortho-phosphoric acid. The volatility depends strongly on the physical state; the monomer can be volatilized, the polymer has a very low vapor pressure.

To illustrate this effect, one gram of DFMDPA was dissolved in 30ml of water and the solution distilled at 100°C. The distillate was collected and titrated. The distillate contained 10^{-4}M DFMDPA. A similar experiment with ortho-phosphoric acid yielded an identical result. Both acids can be volatilized with

steam.

However, both acids readily and reversibly lose water at temperatures above 150°C. At 236°C, DFMDPA forms a dark amber polymer which has a very low vapor pressure. This polymer can be converted back to DFMDPA by boiling in water.

5.4 Electrochemical Behavior

The performance of DFMDPA at the cathode appears to be independent of the relative purity of the compound. DFMDPA cathode performance is not as good as 85% H_3PO_4 at 150°C. The performance of DFMDPA at the anode greatly depends upon the compound's purity. The hydrogen electrode on platinum at 150°C in pure DFMDPA is essentially reversible.

Figure 8 compares the IR free cathode performance on oxygen of DFMDPA with the performance of 85% H_3PO_4 under similar conditions.

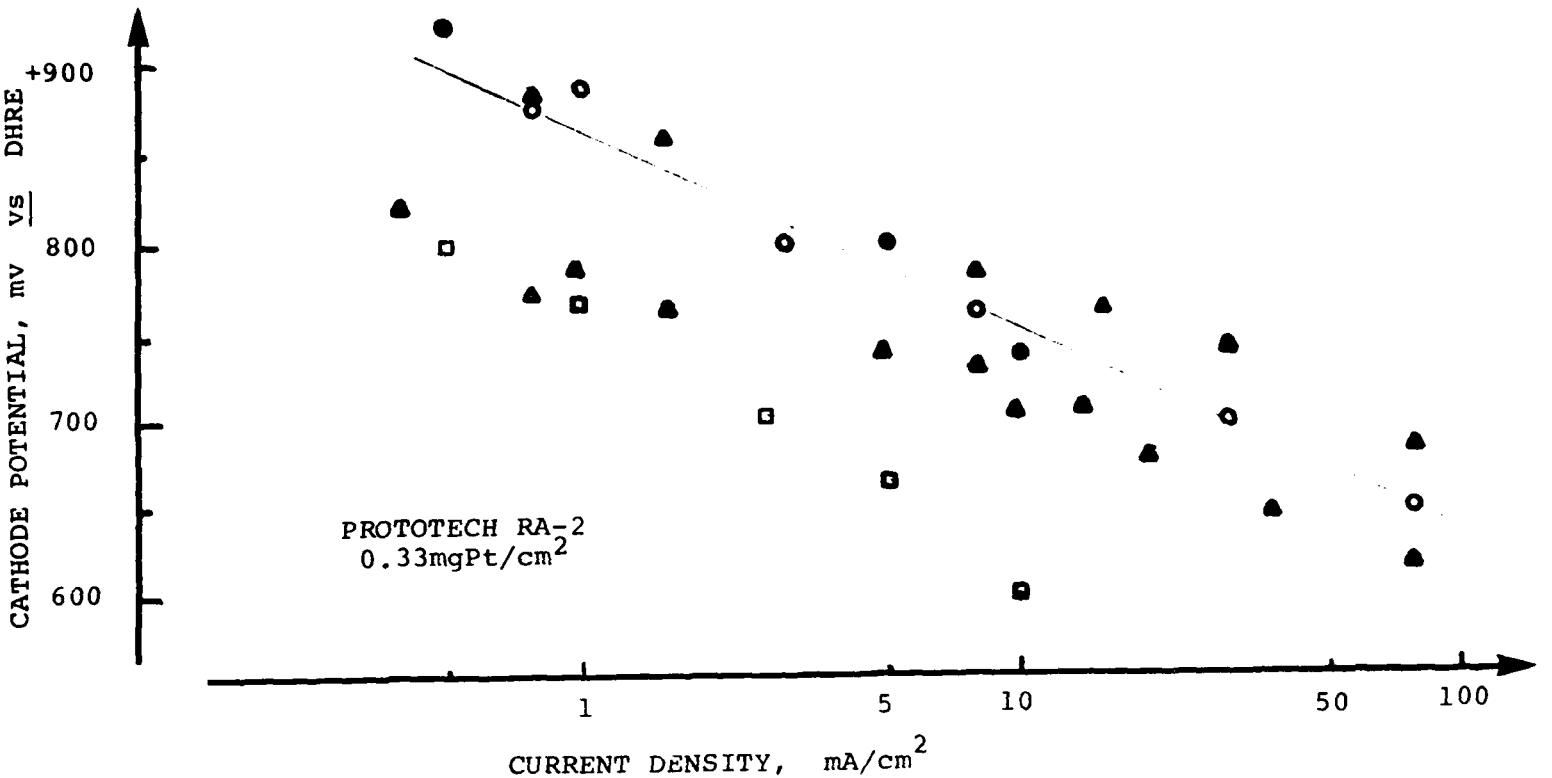
Figure 9 compares the IR free anode performance on hydrogen of DFMDPA with the performance of phosphoric acid under similar conditions.

Tafel slopes for the pure DFMDPA are 130-140mv/decade; Tafel slopes for 90% pure DFMDPA are at 95-110mv/decade.

Open circuit voltages on hydrogen and oxygen for pure DFMDPA at 150°C are about 940mv.

FIGURE 8

IR-FREE CATHODE PERFORMANCE ON DRY OXYGEN



▲ Impure DFMDPA at 150°C

○ Phosphoric Acid at 150°C

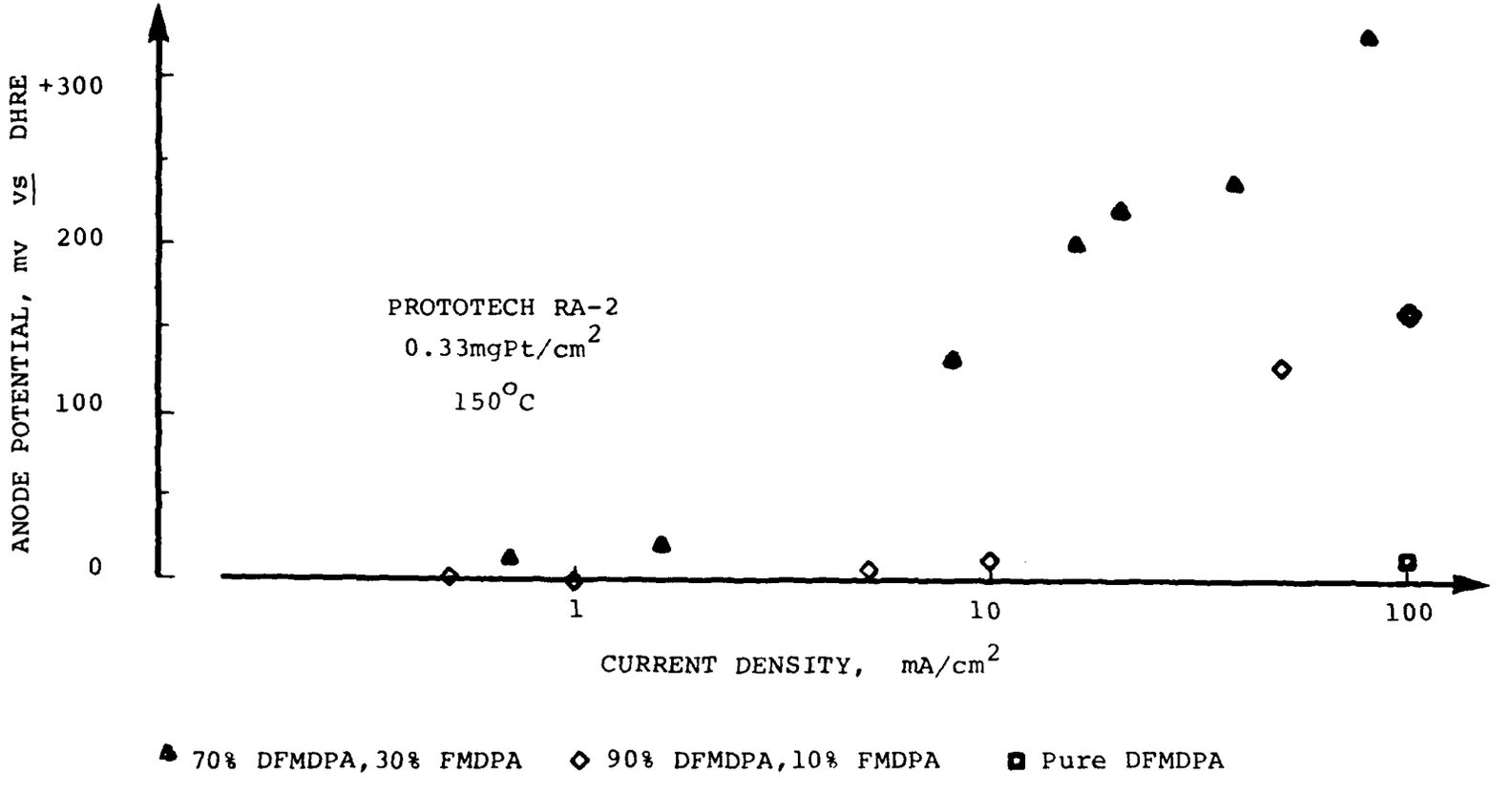
□ Pure DFMDPA at 150°C

▲ Impure DFMDPA at 236°C for 24 hours

● "Phosphoric Acid" at 200°C

FIGURE 9

IR-FREE ANODE PERFORMANCE ON DRY HYDROGEN



6.0 Conclusions

ECO synthesized DFMDPA and attempted to synthesize DFMDSA as an electrolyte to replace phoshoric acid in direct oxidation fuel cells. DFMDPA and DFMDSA may have promise but purer material is needed in order to quantify these benefits.

Electrode optimization may improve the cathode performance of DFMDPA. It does not wet Teflon, but its contact angles are larger than those of phosphoric acid.

7.0 Recommendations

ECO recommends that any future work have three objectives: to synthesize greater than 99% pure DFMDPA and DFMDSA; to determine the behavior of these novel acids in the fuel cell environment and to determine the benefits, if any, of using either DFMDPA or DFMDSA in fuel cells.

Testing of DFMDPA should begin only after pure material has been made. Tests of impure material are very misleading.

8.0 References

1. A.A.Adams and R.T. Foley, J. Electrochem. Soc., 126, 775 (1979)

2. T. Sarada, R.D. Granata, and R.T. Foley, ibid., 125, 1899 (1978)

3. A.A. Adams and H.J. Barger, Jr. Ibid, 121,987 (1974)

4. R.N. Lamp and B.S. Baker, Energy Research Corporation, Electrolyte for Hydrocarbon Air Fuel Cells, Contract DAAK02-73-C-0084

5. J.P. Ackerman and R.K. Steonenberg, Argonne National Laboratory, Evaluation of Electrolytes for Direct Oxidation Hydrocarbon/Air Fuel Cells. Project Order No. MERDC A3101.

6. T. Sarada, J.F. McIntyre and R.T. Foley, The American University, Definition of Chemical and Electrochemical Properties of a Fuel Cell Electrolyte, Contract DAAK70-77-C-0080.

7. S.B. Brummer et al, EIC Corporation, New Electrolytes for Direct Methane Fuel Cells. May 1979. DOE Contract No. DE-AC03-79ET 11321.

8. V.B. Hughes et al, J. Appl. Electrochem., 1, 161 (1977).

9. A.H. Taylor, R.D.Pearce and S.B. Brummer, Trans. Faraday Soc., 66, 2076 (1970)

10. H.W. Fox and W.A. Zisman, J. Colloid Sci., 5,514 (1950).